

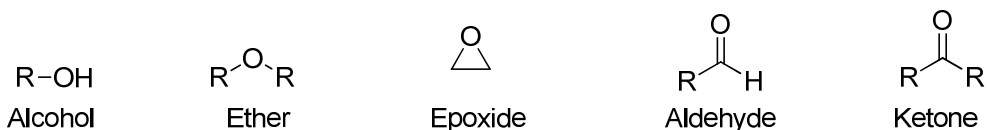
Structure determination

1. Look at the molecular formula. What can you deduce from the molecular formula?

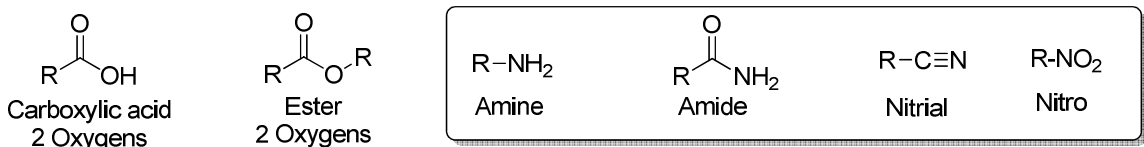
If a compound has the (MF) of $C_5H_{10}O$; Think what functional groups could this molecule have and what functional groups could it not have?

The carbons and hydrogens don't tell you much, but the **one** oxygen is the big clue.

What are some functional groups with one oxygen?

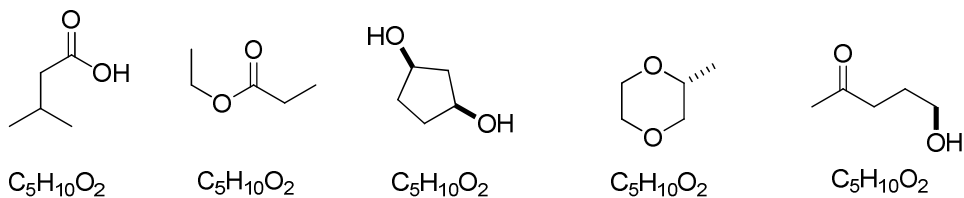


What are some functional groups that would not work?



These functional groups have a Nitrogen and since there is no N in the MF, They don't work

If a compound has the molecular formula $C_5H_{10}O_2$ does that mean that it **HAS** to contain a carboxylic acid or ester? No, it could contain a carboxylic acid or an ester but it could also be two alcohols, two ethers, an alcohol and ketone or an alcohol and aldehyde



Looking at the molecular formula is not meant to be a long drawn out process. It just gives you some early insight what you can or can not have.

2. Figure out the Degrees of unsaturation or the index of hydrogen deficiency (IHD).

Knowing the degrees of unsaturation or IHD will tell you how many rings or π bonds a molecule will have.

Please see the Degrees of unsaturation worksheet for examples on how to calculate the number of π bonds or rings.

3. Look at the chemical tests.

With the invention of ^1H and ^{13}C NMR, chemical tests are not run as frequently as they once were. If chemical tests are given, they give you quick information about the structure.

For example: Compound A (molecular formula $\text{C}_{12}\text{H}_{16}$) is treated with excess $\text{H}_{2(\text{g})}$ in the presence of a Pd catalyst compound B (molecular formula $\text{C}_{12}\text{H}_{22}$) is produced.

What does this tell us about compound A? We know that alkenes and alkynes are chemically reactive towards $\text{H}_{2(\text{g})}$ and Pd, while rings are not. We can hypothesize that compound A has 2 rings and 3 π bonds that were in an alkene or an alkyne.

4. Look at the IR stretches

The IR stretches will tell you what bonds/functional groups you could possibly have in the molecule. Is a huge clue where to start in a problem.

5. Look at your chemical shift.

When faced with a ^1H NMR, look to see if there are any “common” shifts. If you do see a peak in this “common” shift region it does not absolutely mean you have these functional groups.

The easiest one to pick out are:

11-12 ppm the hydrogen of a carboxylic acid

9-10 ppm the hydrogen of an aldehyde

7-8 ppm the hydrogens of an aromatic ring

4.5-5.9 ppm the hydrogens of an alkene.

6. Look for planes of symmetry

If you see a peak with ___ number of hydrogens it is usually a ____ group. This is not always the case but it is helpful to look at a problem.

3 hydrogens = methyl (CH_3)

2 hydrogens = methene (CH_2)

1 hydrogens = methyne (CH)

4 hydrogens = two methene (CH_2) with a plane of symmetry

6 hydrogens = two methyl (CH_3) with a plane of symmetry

9 hydrogens = three methyl (CH_3) C_3 plane of symmetry or a *tert*-butyl group

This correlation is not always true because we can have peaks that overlap. If you have 3 H's in a peak it might be a methyl (CH_3) group but it could also be a methene (CH_2) and a methine (CH) that have the same chemical shift.

7. Think about how functional groups affect chemical shifts

Usually the most downfield signals are the hydrogens that are closest to the oxygens, nitrogens, and the halides. This gives you a clue how to piece the molecule back together with the heteroatoms.

8. Break it down

The worst thing to do in solving a structure is guess. It tends to put ideas in your head that may not be true for the molecule. Break down every hydrogen with its chemical shift and splitting pattern. Then try and put it back together.

Let's work out a problem: What is the structure of Compound X?

Compound X has the MF: C₈H₁₄O₄

It is not reactive to H_{2(g)} and Pd

IR: 2987: 1750, 1252, 1061 cm⁻¹

¹H NMR: 3.7 ppm (s, 6H)
 2.9 ppm (quintet of quartet, 1H)
 2.2 ppm (d, 4H)
 1.1 ppm (d, 3H)

From the molecular formula we can see that the molecule has 2 ° of unsaturation/IHD

The IR tells us that there are no sp² C- bonds plus we know that the molecule is not reactive toward Pd H_{2(g)}: we could think no alkene or alkynes

The IR also tells us that we have a C=O (carbonyl stretch) 1750, a sp² C-O stretch at 1250 and a sp³ C-O stretch at 1061.

If we look at the ¹H NMR we see an integration of 6 H's and 4 H's this tells us that there is a plane of symmetry.

Let's break down the NMR

The peak at 3.7 has 6 H: think 2 -CH₃ groups with a plane of symmetry. They are the most downfield so they are probably attached to an Oxygen.

The peak at 2.9 is probably a methine and has an odd splitting pattern- a quintet of quartets. What would that look like?

The peak at 2.2 is probably a two methylene (CH₂) with a plane of symmetry. It is a doublet so it has only one vicinal H.

The peak at 1.1 is probably a methyl with one vicinal hydrogen

Can you put it together: I'll draw the molecule in the C8H14O4 key doc in the NMR folder